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Profile distribution of mercury in selected urban soils

Profilowe rozmieszczenie rtęci w wybranych glebach miejskich

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Słowa kluczowe: rtęć, gleby miejskie, rozmieszczenie profilowe, antropopresja, Regosole

Abstract
With the expansion of urbanization, the increase of pollutants in air, soil and water is observed. The major source of Hg in urban soils is fossil fuel combustion, and these soils become important indicators of contaminants in the soil environment.
The aim of the research was to determine the distribution of mercury in urban soil profiles on the basis of their physicochemical properties and origin.
Analysed soils come from the city centre of Bydgoszcz, from park and square areas intended for recreation. Research was conducted on four soil profiles: *Mollic Regosol (Technic), Skeletic Regosol (Technic), Eutric Regosol (Loamic), Eutric Regosol (Endoclayic)*. Determined in most profiles artefacts were pieces of bricks, concrete, glass, garbage, slag, asphalt, tar, and charcoals in proportion up to 25% of the volume. In soil samples basic soil parameters and the total content of mercury were determined (using atomic absorption spectrometer AMA-254).
Determined parameters and the total mercury content of analysed soils of Bydgoszcz city were typical for urban areas, and the soils were classified as noncontaminated of this metal (total Hg content 0.009-1.114 $mg \cdot kg^{-1}$, mean 0.218 $mg \cdot kg^{-1}$). In most analysed soils the source of Hg was atmospheric deposition and addition of human-made materials. It was confirmed by significant correlation coefficient -0.415 ($p<0.05$), calculated between Hg content and percent of course fragments (Ø>2mm), among which artefacts were very common. Profile distribution of mercury was mainly the result of antropopression but also the concentration of Hg in parent material. Spatial differentiation of Hg content between tested soil profiles was related with localisation (vicinity of heavy traffic roads).

Streszczenie
Wraz z rozwojem urbanizacji, obserwuje się wzrost zanieczyszczeń powietrza, gleby i wody. Głównym źródłem rtęci w glebach miejskich jest spalanie paliw kopalnych, a gleby stają się ważnymi wskaźnikami zanieczyszczenia środowiska.
Celem przeprowadzonych badań było określenie rozmieszczenia rtęci w profilach gleb miejskich na podstawie ich właściwości fizyko-chemicznych i genezy.
Badane gleby pochodziły z centrum Bydgoszczy, z obszarów parków i skwerów przeznaczonych na cele rekreacyjne. Badania przeprowadzono na czterech profilach glebowych: *Mollic Regosol (Technic), Skeletic Regosol (Technic), Eutric Regosol (Loamic), Eutric Regosol (Endoclayic)*. Stwierdzone w większości profili glebowych artefakty były kawałkami cegieł, betonu, szkła, odpadów, żużla, asfaltu, smoły i węgla drzewnego w ilości dochodzącej do 25% objętości próbki. W badanych próbkach oznaczono podstawowe parametry glebowe oraz całkowitą zawartości rtęci (przy użyciu spektrometru absorpcji atomowej AMA-254).
Oznaczone parametry glebowe oraz całkowita zawartość rtęci w badanych glebach Bydgoszczy były typowe dla obszarów miejskich, a gleby sklasyfikowano jako niezanieczyszczone tym metalem (całkowita zawartość Hg 0,009-1,114 $mg \cdot kg^{-1}$, średnio 0,218 $mg \cdot kg^{-1}$). W większości analizowanych gleb źródłem rtęci była depozycja atmosferyczna, jak również obecność domieszek. Potwierdził to istotny statystycznie współczynnik korelacji -0,415 ($p <0,05$), obliczony pomiędzy zawartością Hg i udziałem części szkieletowych, wśród których artefakty stanowiły znaczną część. Rozmieszczenie profilowe rtęci było głównie wynikiem antropopresji ale także zawartości Hg w skale macierzystej. Przestrzenne zróżnicowanie zawartości Hg między badanymi profilami glebowymi, było związane z ich lokalizacją (głównie sąsiedztwem dróg o dużym natężeniu ruchu).

1. INTRODUCTION

According to Bockheim [1974], the urban soil is a soil material having a nonagricultural, man-made surface layer of more than 50 cm thickness that has been produced by mixing, filling or by contamination of land surfaces in urban and suburban areas. Craul [1999] noted among others several characteristics of these soils like great vertical and spatial variability, modified soil structure, modified soil reaction (usually elevated), modified soil organism activity or the presence of anthropic materials and other contaminants. All these are the effect of anthropogenic activities rather than soil formation processes. With the expansion of urbanisation, the increase of pollutants in air, soil and water is observed [Wong et al. 2006]. Urban soils are important indicators of contaminants such as Hg in the soil environment [Solgi et al. 2014].
Mercury has been recognised as a global contaminant due to its high toxicity, persistency in the environment and ability to

undergo long distance transportation in the atmosphere [Liu et al. 2012]. This element comes from natural and anthropogenic sources, whereas in city areas the most important is the latter source. Among others (like mining and smelting of ores, chlor-alkali plants, waste incineration, use of agricultural fertilisers and fungicides, land spreading of sewage sludge), the most significant source of Hg in urban soils is fossil fuels combustion [Alloway 1995; Remy et al. 2003]. The burning of coal, gasoline, diesel and LPG (Liquefied Petroleum Gas) fuels is considered the major source of emissions of mercury. LPG fuel showed the highest Hg concentration, followed by gasoline and diesel. Hg in the exhaust gas is mostly in elemental form (Hg^0) [Rodrigues et al. 2006; Won et al. 2007]. Moreover, there is a significant positive correlation between atmospheric and soil Hg concentrations in urban soils [Wang et al. 2003].
The aim of the research was to determine the profile distribution of mercury in horizons of typical Polish city soils on the basis of their physico-chemical properties and origin.

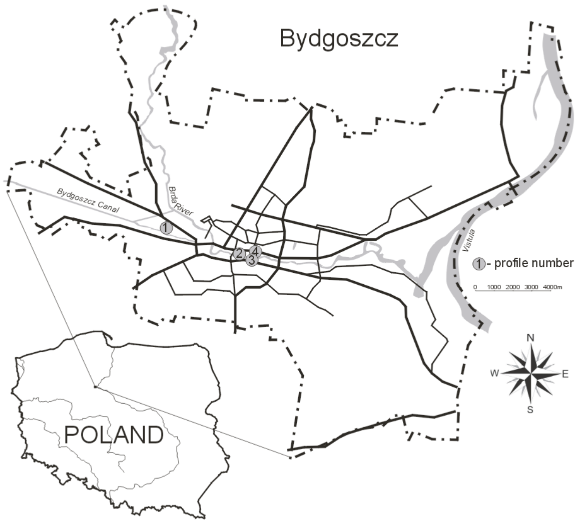

Fig. 1. Localisation of investigated soil profiles

2. MATERIALS AND METHODS

Analysed soil profiles come from the Bydgoszcz city, located in the north-western part of the Toruńska Basin and in the lower part of the Brda River Valley. This area is covered by sediments of various origin, texture and ages, like Pliocene clays and silts, Pleistocene tills, sands and gravels [Kondracki 2000; Kozłowska, Kozłowski 1990].
The soil pits were dug out in the centre of the city, on both banks of the Brda River (Fig. 1.). All investigated areas are parks and squares intended for recreation. Profile no 1 – *Mollic Regosol (Technic)*-– was located on the Bydgoszcz Canal Park. Identified horizons upto 80 cm deep were sandy textured with a high proportion of coarse fragments of urban and other human-made materials, ranging from 6 to 25% (pieces of bricks, concrete, glass, garbage, textile). What was found belo, was a rather homogeneous sandy material with no artefacts and water table at a depth of 140 cm. Profile no 2 – *Skeletic Regosol (Technic)* – comes from the square at the Bernardyńska Street with artefacts exceeding 20% by volume (mainly pieces of bricks, concrete and glass) and inset of 99% sand separates at 15 – 25 cm depth. Profile no 3 – *Eutric Regosol (Loamic)* – was the soil with the most limited human impact (no artefacts) and the lowest proportion of course fragments (1%) in whole profile. It was located on Freedom Hill City Park underneath old deciduous trees. Profile no 4 – *Eutric Regosol (Endoclayic)* – was situated on the Brda promenade, close to the Central Bus Station on Jagiellońska Street. It was the most diversified soil profile with horizons of different texture (from sands to clays) and proportion of artefacts (0-22%). Soils were classified according to the World Reference Base for Soil Resources 2014 [IUSS 2014].
Soil samples were collected from each horizon and layer, analysis was conducted according to international standards [Van Reeuwijk 2006]. The following soil parameters were determined: texture using hydrometer method (USDA), soil organic carbon (TOC) by wet oxidation in potassium dichromate and sulphuric acid, pH in H_2O, and in 1M KCl, and carbonates content. The total content of mercury was determined in homogenised solid soil samples after thermal decomposition in 700°C using single-purpose atomic absorption spectrometer AMA-254. Results were calculated from three replications with standard deviation not exceeding 5%, and validated on certified material (Tab. 1.). Determined results were processed in STATISTICA 8.0.

Table 1. Parameters of certified material (Hg)

Certified material	Certified value [μg·kg^{-1}]	Determined value [μg·kg^{-1}]	Standard deviation [%]	Number of replications
SO-4*	30 ± 6	36.34 ± 0.43	0.8057	6

* - Certificate of analysis, 1995: Reference soil sample SO-4. Canada Center for Mineral and Energy Technology

3. RESULTS AND DISCUSSION

Analysed soils were very diversified in texture both because of the difference of parent materials and different human impact. *Eutric Regosol (Loamic),* profile no 3, was the soil of almost homogeneous texture of sandy clay loam in all horizons with clay of 23–26%, silt 22–27% and sand 49–52% (Tab. 2.). Moreover, it was the only soil without artefacts in whole profile. *Mollic Regosol (Technic)*, profile no 1, was formed from the sand of 98–99% of sand separates. Surface and subsurface horizons (0-80cm) with the texture of sandy loams were enriched in pieces of bricks, concrete, glass, and garbage up to 25% (Bhu1). *Skeletic Regosol (Technic)*, profile no 2, was loamy sand with inset of sand at 15-25 cm depth. It was probably human made layer as a residue of old pavement or other construction. In all profiles the presence of artefacts was noticed, excided 20% by volume (mainly pieces of bricks, concrete and glass). *Haplic Regosol (Endoclayic)*, profile no 4, was formed of horizons from sands, via sandy loams to clays. Artefacts were noticed only in two horizons (Au and Bu2) as fragments of bricks, glass, slag, asphalt, tar and charcoals.
In analysed soils pH was neutral and alkaline with pH H_2O ranging from 7.1 to 8.9 and pH KCl from 6.5 to 8.5. It was

Table 2. Selected soil parameters and total mercury content in analysed soil profiles

No	Horizon	Depth	Particle size distribution			Texture class	pH		$CaCO_3$	TOC	Hg
			2mm-50µm	50µm-2µm	< 2 µm		H_2O	KCl			
		[cm]	[%]			USDA			[%]	[g·kg^{-1}]	[mg·kg^{-1}]
Mollic Regosol (Technic)											
1.	Au	0-6	77	12	11	SL	7.2	7.1	5.6	37.5	0.165
	Bhu1	6-24	76	11	13	SL	7.8	7.5	4.3	21.5	0.151
	Bhu2	24-51	77	15	8	SL	7.6	7.5	7.5	36.0	0.164
	Bhu3	51-80	88	4	8	LS	7.4	7.3	1.1	11.0	0.129
	Bw	80-98	95	2	3	S	7.3	7.2	0.3	1.9	0.015
	C	98-126	98	1	1	S	7.4	7.3	0.3	0.3	0.009
	Cg	126-150	99	1	0	S	7.7	7.5	0.3	0.1	0.016
Skeletic Regosol (Technic)											
2.	Au	0-15	86	8	6	LS	7.8	6.9	1.1	25.1	0.327
	Bu1	15-25	99	1	0	S	8.0	7.8	0.7	0.1	0.023
	Bhu2	25-55	85	6	9	LS	7.9	7.6	3.0	10.1	0.945
	Bhu3	55-150	86	6	8	LS	8.0	7.7	1.5	10.7	1.114
Eutric Regosol (Loamic)											
3.	A	0-8	52	25	23	SCL	7.1	6.5	0.6	44.9	0.114
	A/B	8-33	52	22	26	SCL	8.1	7.2	1.3	4.1	0.063
	Ck1	33-49	49	27	24	SCL	8.3	7.3	2.2	1.1	0.059
	Ck2	49-97	49	27	24	SCL	8.3	7.5	4.6	2.6	0.046
	Ck3	97-150	50	27	23	SCL	8.1	7.5	2.3	0.6	0.047
Eutric Regosol (Endoclayic)											
4.	Au	0-15	77	15	8	SL	8.0	7.4	4.5	111.0	0.275
	Bu1	15-28	98	2	0	S	8.9	8.5	4.2	0.1	0.011
	Bhu2	28-36	93	5	2	S	8.0	7.4	0.7	24.4	0.613
	Bu3	36-42	96	4	0	S	8.2	7.9	0.3	0.6	0.024
	Buw	42-65	97	3	0	S	8.0	7.7	0.4	1.6	0.039
	Ck1	65-109	9	11	80	C	7.6	7.1	2.8	2.4	0.074
	Ck2	109-160	6	17	77	C	7.7	7.1	0.9	0.4	0.764
	2Ck	160-200	72	15	13	SL	7.4	7.1	1.8	17.3	0.033

S – sand, SL - sandy loam, LS – loamy sand, SCL – sandy clay loam, C – clay.

mainly the result of building rubble addition (artefacts) with the exception of profile no 3, where parent material was rich in carbonates (2.2-4.6%).

The content of organic carbon was also the effect of both natural processes (surface accumulation) and anthropopression. The content of TOC ranged from 0.1 to 111.0 g·kg^{-1} of soil. The highest values were determined in surface horizons, but in profile no 2 and 4 also the deepest horizons were significantly enriched in organic matter. Profile and spatial variation of organic carbon content in analysed soils may be the result of addition of peat or compost used in the treatment of city lawn sides as well as land levelling or works related with soil mixing [Craul 1999].

The total content of mercury ranged from 0.009 to 1.114 mg·kg^{-1}, with a mean of 0.218 mg·kg^{-1}, and did not exceed the limit of

2 mg·kg^{-1} due to the relevant Polish Regulation [Regulation… 2002]. These values were typical for other urban areas across the world. In such cities like Jakobstad (0.011-0.093 mg·kg^{-1}), Palermo (0.04-6.96 mg·kg^{-1}), Oslo (<0.01-2.30 mg·kg^{-1}), Trondheim (<0.2-4.49 mg·kg^{-1}), Cornwall (0.04-5.10 mg·kg^{-1}), Beijing (0.007-8.487 mg·kg^{-1}), Berlin (0.19 mg·kg^{-1}) or Amursk (0.004-16.65 mg·kg^{-1}) the range of Hg content was wide and mostly related to localisation in the city (distance from potential source of contamination) and land use (e.g. park, garden, roadside) [Birke, Rauch 2000; Kot, Matyushkina 2002; Li et al. 2010; Manta et al. 2002; Peltola, Astrom 2003; Reimann, Caritat 1998; Sherbin 1979; Solgy et al. 2014; Tijhuis et al. 2002]. In the previous research of Bydgoszcz city soils also the same tendency was noticed (0.01-4.03 mgHg·kg^{-1}) [Różański, Dąbkowska-Naskręt 2011]. Profile distribution of mercury was typical for not disturbed, natural soils with surface accumulation only in *Mollic Regosol* (profile no 3). Hg content was decreasing with depth, and in this case atmospheric deposition should be considered as the only source of mercury. In all other analysed soils the source of Hg was atmospheric deposition and addition of materials potentially contaminated with mercury compounds. It was confirmed by the significant correlation coefficient between Hg content and percent of course fragments (Ø > 2 mm), among which artefacts were very common (0.415; $p<0.05$). It was especially noticed in Bhu2 horizon of profile no 4, with the presence of slag, asphalt, tar, and charcoals fragments (course separates 21%). Generally, it was characteristic for Bhu horizons of profiles no 1 and 2. In all these horizons high values of Hg content were observed (as well as TOC). There might (not statistically confirmed) be a relation between the mercury content and the organic carbon content. It is commonly known that the crucial parameter in mercury transformation in the environment is the content of organic matter [Dmytriw et al. 1995; Henderson et al. 1998].

Soil conditions usually are favourable for the formation of inorganic Hg compounds, limiting its mobility. Adsorption of Hg(II) on clay minerals and oxides is more favourable at a higher pH. Alkaline conditions and low organic matter content in studied soils favoured the retention of Hg species by soil. Furthermore, low organic matter content decreases the formation of soluble organic complexes [Lafont et al. 2013]. It seems that in investigated soils mobility of mercury, because of neutral and alkaline conditions and relatively high content of organic matter, is rather low.

In urban areas the major source of Hg in atmosphere, and as a consequence in soils, is fossil fuel combustion [Klojzy-Karczmarczyk 2013; Rodrigues et al. 2006; Wang et al. 2003; Won et al. 2007]. It was reflected in analysed soils, where the highest values were determined in close vicinity of heavy traffic roads (profile no 2) and Central Bus Station (profile no 4).

There was no relationship noticed between Hg content and other soil parameters in analysed soil profiles (no significant correlation coefficients).

4. CONCLUSIONS

1. The total mercury content and soil parameters of analysed profiles of Bydgoszcz city were typical for urban areas, and the soils were classified as noncontaminated of this metal.
2. The major potential source of Hg in these soils was atmospheric deposition and addition of contaminated materials (artefacts).
3. Profile distribution of mercury was mainly the result of impact of human activity but also the concentration of Hg in parent material.
4. Spatial differentiation of Hg content between tested soil profiles was related with localisation (vicinity of heavy traffic roads).

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